

QMCPACK Training Program

Argonne National Laboratory

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Quantum Monte Carlo Methods Molecular Calculations

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Outline

- Basics
- Trial Wave-functions
- (Brief) Intro. To (some) Quantum Chemistry
- Survey of Recent Applications
- Future Outlook

Today we will focus on finite systems!
Tomorrow focus will be on solids!

First-Principles Computational Physics/Chemistry

Schrodinger Equation
Theory of electrons and ions

Chemistry:

- chemical reactions
- molecular properties
- bonding patterns/formation
- solvation properties
- surfaces

Exotic electronic phases:

- Superconductivity
- Magnetism
- Charge ordering

Thermodynamics:

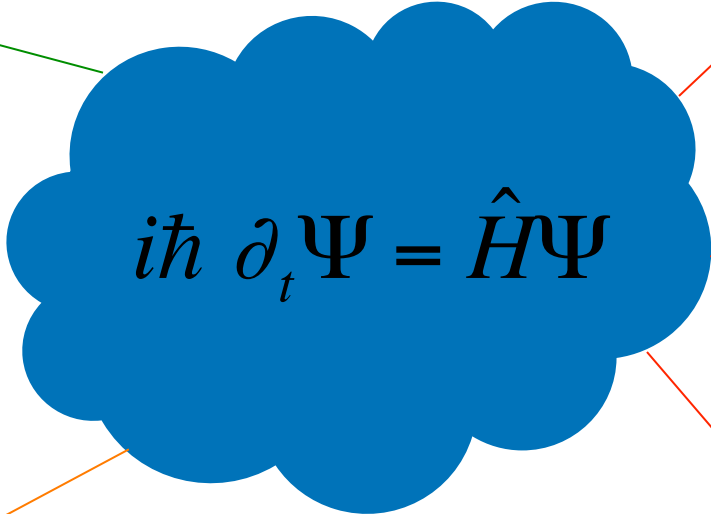
- crystal structures
- phase transitions
- strength
- defects and dislocations

Plasmas:

- equilibrium prop.
- kinetics
- instabilities
- shocks

Optical and Transport Properties:

- spectra
- conductivity
- viscosity
- diffusion


$$i\hbar \partial_t \Psi = \hat{H} \Psi$$

Born-Oppenheimer Approximation

$$i\hbar \partial_t \Psi(\vec{r}, t) = \hat{H} \Psi(\vec{r}, t)$$

$$\hat{H} = -\frac{\hbar^2}{2m} \sum_i \vec{\nabla}_i^2 + \sum_{i < j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} - \sum_{i, I} \frac{Z_I e^2}{|\vec{r}_i - \vec{R}_I|} - \frac{\hbar^2}{2M} \sum_I \vec{\nabla}_I^2 + \sum_{I < J} \frac{Z_I Z_J e^2}{|\vec{R}_I - \vec{R}_J|}$$

$m_{elec} \ll m_{prot} \rightarrow$ they move on different time scales

$$\Psi(\vec{r}, \vec{R}) = \sum_k \xi_k(\vec{R}) \sum_q \psi_{k,q}(\vec{r}, \vec{R})$$

BO leads to independent solutions for electrons and ions (different approximations) !!!

$$\left[-\frac{\hbar^2}{2m} \vec{\nabla}^2 + V_{e-e}(\vec{r}, \{\vec{R}\}) + V_{e-I}(\vec{r}, \{\vec{R}\}) \right] \psi_q(\vec{r}) = E_q^{BO} \psi_q(\vec{r})$$

If finite gap between ground state and 1st excited state, assume electrons remain in the ground state! (Electrons at T=0 K !)

$$\left[-\frac{\hbar^2}{2M} \vec{\nabla}_I^2 + V_{I-I}(\vec{R}) + E_{BO}(\vec{R}) \right] \xi(\vec{R}) = E \xi(\vec{R})$$

Solve ionic problem !



First-Principles Electronic Structure Theory

$$\left[-\frac{\hbar^2}{2m} \vec{\nabla}^2 + V_{e-e}(\vec{r}, \{\vec{R}\}) + V_{e-I}(\vec{r}, \{\vec{R}\}) \right] \psi_q(\vec{r}) = E_q^{BO} \psi_q(\vec{r})$$





Only input:
• $N\alpha$ $R\alpha$, $Z\alpha$



Density Functional Theory

-  Mean-field cost, well developed codes, easy to learn, HPC.
-  Hard to improve, accuracy is unknown, fails for correlated problems!

Quantum Chemistry Methods

-  Very accurate and robust, well developed codes.
-  High cost ($>N^5$), very hard for solids, complicated, no HPC.

Quantum Monte Carlo

-  Accurate, improvable, trivially parallelizable, ok scaling (N^3)
-  High cost, human time intensive, small community, problems at high Z .

Why QMC?

- QMC: stochastic solution of the Schrodinger equation
 - Exact for bosonic problems
 - Sign problem for fermions: approximations required
- Stochastic methods offer the main alternative for exact results in classical many-particle problems.
 - Can we reach the same scenario on fermionic problems?

Some Strengths

- Many-body problem
 - Direct treatment of electron correlation
 - Variational results: Systematically improvable solutions
 - Framework for accurate (possibly exact) results
- Low scaling with particle number
- Efficient use of massively parallelized resources
 - > 90% efficiency on > 250k CPU
 - Efficient GPU implementation

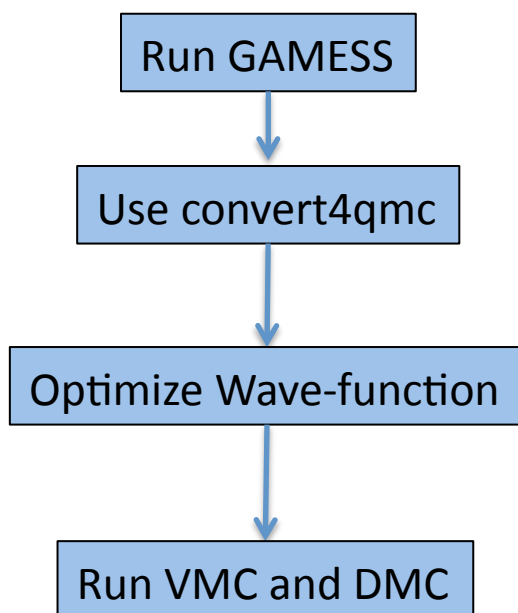
Some Weaknesses

- Many-body problem
 - Strong size effects in solids
 - Hard to simplify problem (symmetry, core, etc)
 - High computational cost
- Fixed node approximation hard to control
- High learning curve
 - Small community
 - Slow and uncoordinated development

Basic Workflow

As we will see in the afternoon, QMCPACK calculations on finite systems are easy!

- The converter takes care of most of the work!
- Basic optimization block will work with almost any wave-function!
- Good ECP libraries exist! Grab one and start calculations!
- For many problems, standard SJ wave-function is good enough. Should always start here.



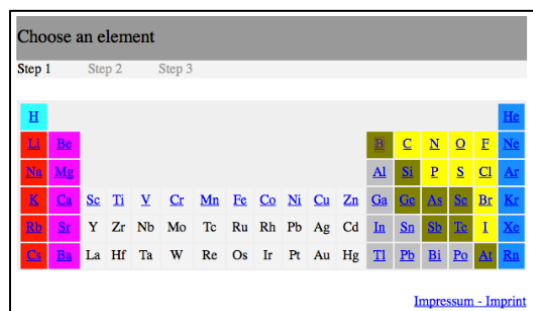
```
rungms HF.inp > HF.out
convert4qmc -gamessAscii HF.out
qmcapp optm.xml
qmcapp vmc_dmc.xml
qmca
```

Effective Core Potentials for Chemistry

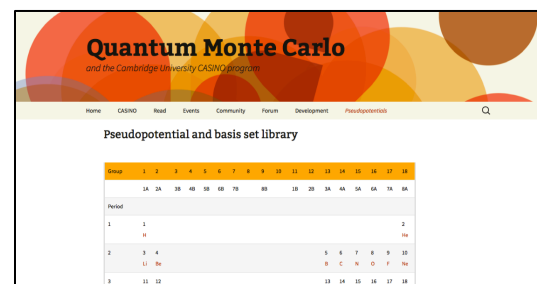
$$V_{\text{Coulomb}} = - \sum_{i,\alpha} \frac{Z_{\alpha} e^2}{|\vec{r}_i - \vec{R}_{\alpha}|} \longrightarrow V_{\text{ECP}} = V_{\text{loc}}(r) + \sum_{l,m} V_l(r) \delta(r - r') Y_{l,m}(\hat{r}) Y_{l,m}^*(\hat{r}')$$

$$V_l = \sum_i c_i r^{n_i} e^{-\alpha_i r^2}$$

- Remove core electrons.
- Typically expanded with Gaussians.
- Should be used with corresponding basis sets if available!
- 2 well tested ECP collections for molecules: BFD and Casino.



More
Tomorrow!



Gaussian, Gamess and Molpro format.
<http://burkatzki.com/pseudos/index.2.html>

Tabulated, Gaussian, Gamess format.
<http://vallico.net/casinoqmc/pplib/>

Trial Wave-Functions

What do I need to evaluate?

For VMC, DMC: $\left\{ \Psi(\vec{r}), \vec{\nabla}_i \ln|\Psi(\vec{r})|, \nabla_i^2 \ln|\Psi(\vec{r})| \right\}$

For optimization: $\left\{ \nabla_\alpha \Psi(\vec{r}), \nabla_\alpha \vec{\nabla}_i \ln|\Psi(\vec{r})|, \nabla_\alpha \nabla_i^2 \ln|\Psi(\vec{r})| \right\}$

- Critically important in all QMC calculations:
 - Uncontrolled approximations depend on Ψ_T
 - Systematic effects also depend sensitively on Ψ_T
 - Defines cost and accuracy!
- QMC can handle complicated wave-functions.
 - If we can evaluate it in real space, we can use it!

Basis Sets for Molecules

- Single particle states are expanded in a linear combination of atom-centered basis functions.

$$\phi_k(\vec{r}_i) = \sum_{\mu, I} c_{\mu}^k \xi_{\mu}(\vec{r}_i - \vec{R}_I)$$

Slater-type Orbitals (STO)

$$\xi_{n,l,m}(r, \theta, \varphi) = N r^{n-1} e^{-\alpha r} Y_{l,m}(\theta, \varphi)$$

Spherical

Cartesian

Gaussian-type Orbitals (GTO)

$$\xi_{n,l,m}(r, \theta, \varphi) = N r^l e^{-\alpha r^2} Y_{l,m}(\theta, \varphi)$$

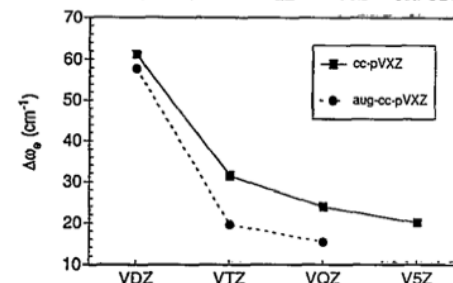
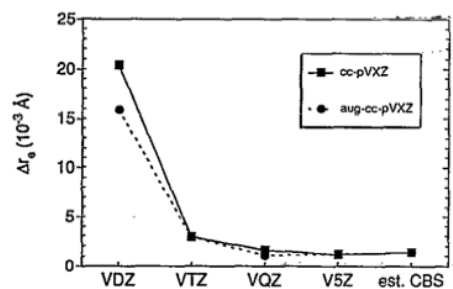
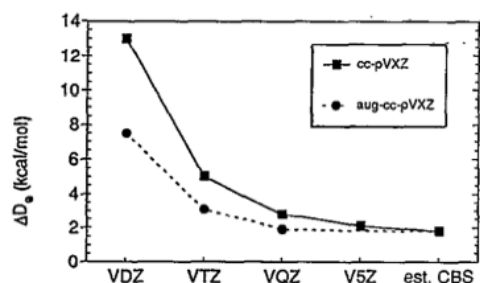
$$\xi_{n_x, n_y, n_z}(\vec{r}) = N r^l e^{-\alpha r^2} x^{n_x} y^{n_y} z^{n_z}$$

- Gaussians are the most popular basis function. Gaussian integrals can be performed analytically!
 - GTOs have a poor shape close to the nucleus. Fixed linear combinations (contractions) are used to improve the shape of the basis (so that basis functions resemble realistic atomic orbitals)
- Internally, QMCPACK transforms all radial basis functions into a numerical representation with cubic (or quintic) Spline interpolation.
 - Faster evaluation! Cleaner code!
 - Both cartesian and solid harmonics for angular representation.

Basis sets

- Basis sets are (almost) ubiquitous in molecular calculations.
- Considerable effort has been put in developing hierarchical basis sets of increasing accuracy.
 - Molecular properties converge slowly basis set size.
- Typical basis sets:
 1. Minimum basis sets: 1 basis function per electron pair
 2. Pople basis sets: STO-nG, 6-31 G, etc.
 3. Correlation consistent basis sets: cc-pVXZ, aug-cc-pVXZ, cc-pCVXZ, etc; where X is {D, T, Q, 5, etc}.
 4. Atomic Natural Orbital basis sets: e.g. ANO-TZ

K. Peterson, J. Chem. Phys. 99, 1930 (1993).



HF energy converges exponentially fast: $E_{HF}(X) \approx E_{HF}^{CBS} + ae^{-cX}$

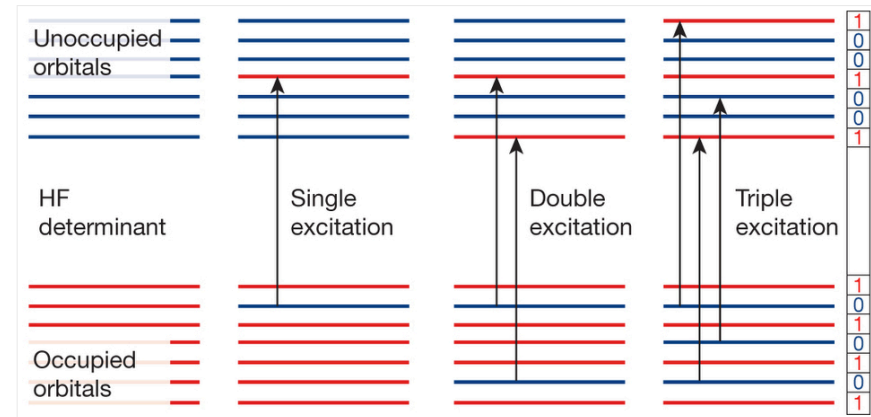
Correlation energy converges very slowly: $E_{corr}(X) \approx E_{corr}^{CBS} + aX^{-3}$

Slater Determinants

$\{\phi_k\}$ Single particle orbital set, e.g. DFT, HF. Let $M_{k,i} = \phi_k(\vec{r}_i)$

$$D(\vec{r}) = \det(M) = \det \begin{pmatrix} \phi_1(\vec{r}_1) & \dots & \phi_1(\vec{r}_N) \\ \vdots & \ddots & \vdots \\ \phi_N(\vec{r}_1) & \dots & \phi_N(\vec{r}_N) \end{pmatrix}$$

$$\frac{\vec{\nabla}_i D}{D} = \sum_k M_{ik}^{-1} \vec{\nabla} \phi_k(\vec{r}_i) \quad \left| \quad \frac{\nabla_i^2 D}{D} = \sum_k M_{ik}^{-1} \nabla^2 \phi_k(\vec{r}_i) \right.$$



Typical operation cost:

- Evaluation of each $\{\phi_k\}$: N
 - With localized orbitals or splines: $O(1)$
- Inverse and determinant of M : N^3
- Single particle update to M^{-1} : N^2
- Evaluate all gradients and laplacians:
 - From scratch: N^3
 - With known inverse: N^2
 - For a single particle: N

- In a basis set, Slater determinants are a complete many-body basis.
 - Leads to combinatorial number of determinants. Given M orbitals, all possible ways to choose N .
- Hartree-Fock state is the best single determinant representation of the system.
 - Typically, methods are based on excitations out of HF determinant.

Figure from: G. H. Booth, Nature 493, 365–370 (2013).

Configuration Interaction

- Full CI: exact diagonalization of Hamiltonian in determinant basis

- Scales exponentially with system size.
- Exact solution within given basis set!

$$|\Psi\rangle = \sum_{i \in \binom{M}{N}} C_i |D_i\rangle \longrightarrow H_{i,j} C_j = \epsilon C_i$$

- Truncated CI: include all determinants up to a given excitation from HF.

$$\Psi = \sum_{i \in \{S, D, \dots\}} C_i |D_i\rangle$$

- Better scaling with system size: N^{4+k} , when up to k excitations are included.
- It is not size extensive! (Accuracy is not uniform as a function of system size)
 - Can you think why?
- Complete Active Space (CAS)-CI: Instead of limiting by excitations, limit the number of active orbitals. CAS-CI means full-CI on a subset of the single particle orbitals.
 - Still scales exponentially, but on a much reduced space.
 - Useful (needed) in strongly correlated systems.

Electronic Correlation: Dynamic vs Static

In simple terms:

- **Static (or strong) correlation:** Contribution from important determinants! Their contribution to the total many-body wave-function is large, e.g. > 0.1 .
 - If only HF has large weight, the system is considered single reference. In this case, perturbation theory based on HF should work!
 - If multiple determinants have large weights, they must all be considered in perturbation theory, e.g. MR-CI.
 - Typically related to nearly degenerate low-energy orbitals. Multiple Slater determinants are close in energy, true many-body state has contributions from many of them.
 - Symmetry constraints can also introduce static correlation!
 - RHF can not dissociate into fragments! UHF can!
- **Dynamic Correlation:** Combined contribution of exponentially large number of “unimportant” determinants.
 - Main contribution from short-range correlations (electrons repel each other!)
 - Other contributions like dispersion interactions!

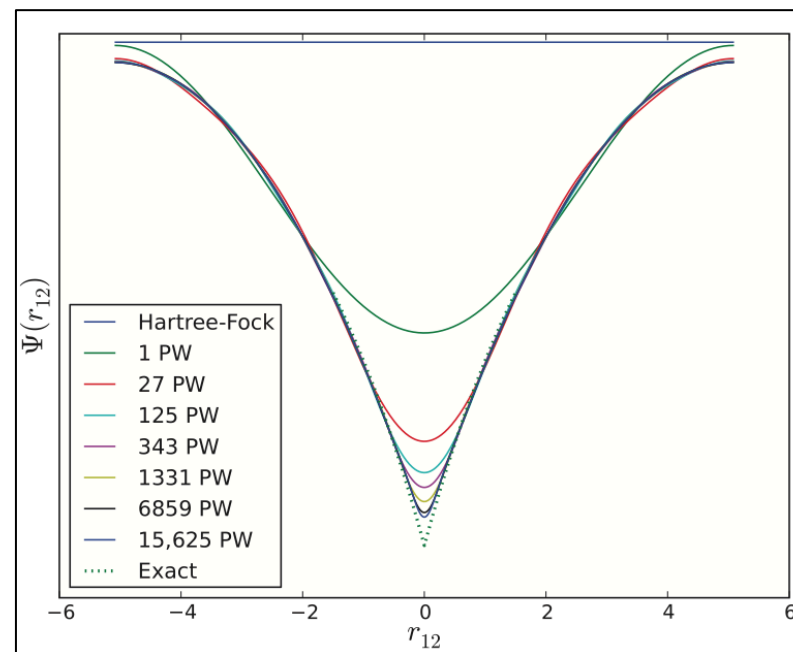
Jastrow Functions - I

$$\Psi_T(\vec{r}) = D(\vec{r}^\uparrow)D(\vec{r}^\downarrow)e^{J(\vec{r})}$$

Slater-Jastrow

$$\left. \frac{\partial \ln(\Psi(\vec{r}))}{\partial r_{ij}} \right|_{r_{ij} \rightarrow 0} = \begin{cases} -1/2 & \neq \text{spin} \\ -1/4 & = \text{spin} \\ -Z & \text{e-I} \end{cases}$$

Cusp conditions must be satisfied exactly to prevent divergence of the local energy.



- Correlates electrons explicitly. Excellent for dynamic correlation!
 - Constructed to satisfy e-e and e-I cusp conditions.
 - Very hard to treat in deterministic methods. Need for multi-electron repulsion integrals!
- Only bosonic correlation. Does not modify nodes!
 - No improvement to fixed-node error.

Gruneis, et al., JCP **139**, 084112 (2013).

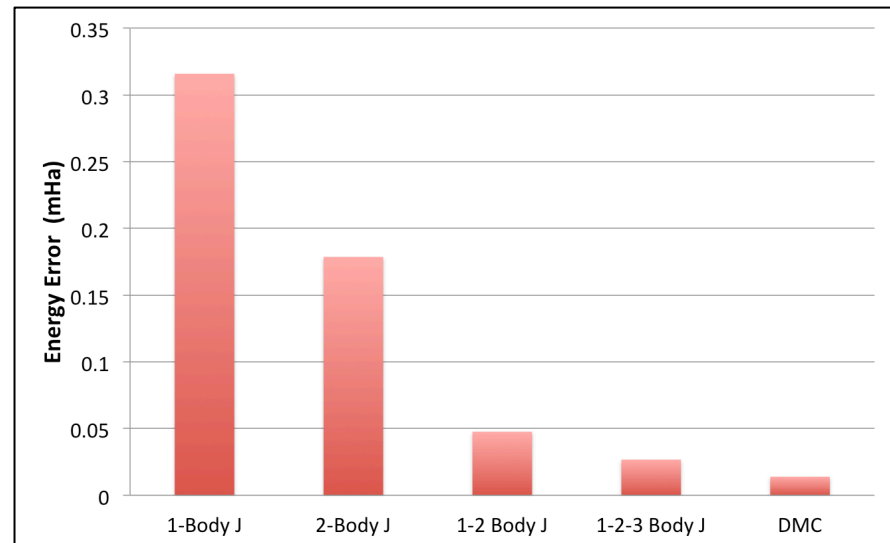
Jastrow Functions - II

$$J(\vec{r}) = u^{e-I} + u^{e-e} + u^{e-e-I} + u^{e-e-e} + \dots$$

$$u^{e-I} = \sum_k \sum_{i,I} c_k f_k(\vec{r}_i - \vec{R}_I)$$

$$u^{e-e} = \sum_k \sum_{\alpha,\beta} \sum_{i_\alpha,j_\beta} c_k f_k^{\alpha,\beta}(\vec{r}_{i_\alpha} - \vec{r}_{j_\beta})$$

$$u^{e-e-I} = \sum_{k,I} \sum_{\alpha,\beta} \sum_{i_\alpha,j_\beta} c_k f_k^{\alpha,\beta}(\vec{r}_{i_\alpha,I}, \vec{r}_{j_\beta,I}, \vec{r}_{i_\alpha,j_\beta})$$



- Each term is expanded with an atom-centered basis set
- Variational parameters fully optimized with VMC.
- If needed, radial functions must satisfy cusps.

Jastrow Functions - III

In addition to standard basis functions like exponentials, gaussians and polynomials, other popular functions used to expand the Jastrow are:

$$f(r_{ij}) = \frac{ar_{ij}}{1 + br_{ij}}$$

Pade functions

$$f(r_{ij}) = \frac{1 - q(r_{ij} / rcut)}{1 + b q(r_{ij} / rcut)}$$

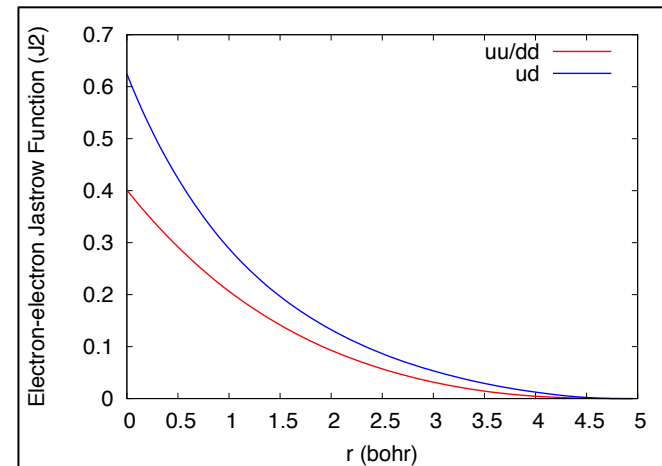
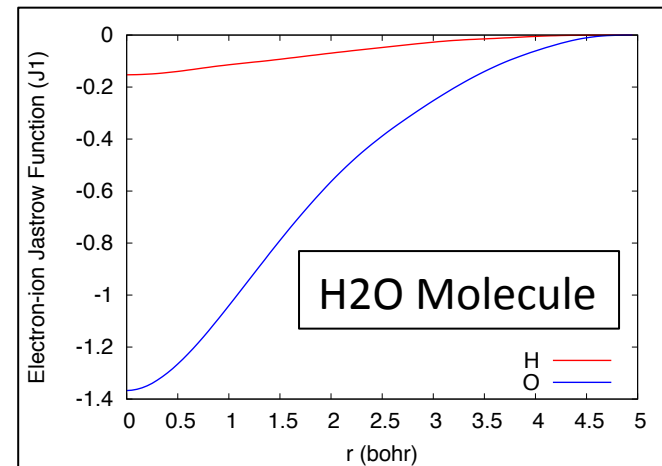
$$q(r) = r^2(6 - 8r + 3r^2)$$

Polynomial-Pade functions

$$f(r) = \sum_{k=i-1}^{k+2} b^{k,3}(x) p_k$$

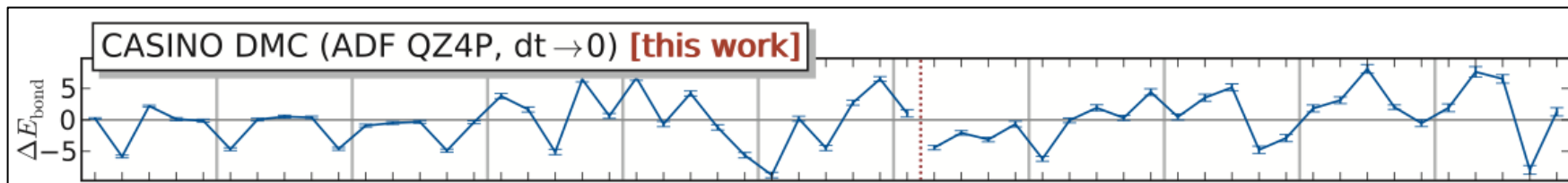
B-splines

$b^{k,3}(x)$ = piecewise cubic polynomials



QMCPACK can use numerical basis functions (splines)!

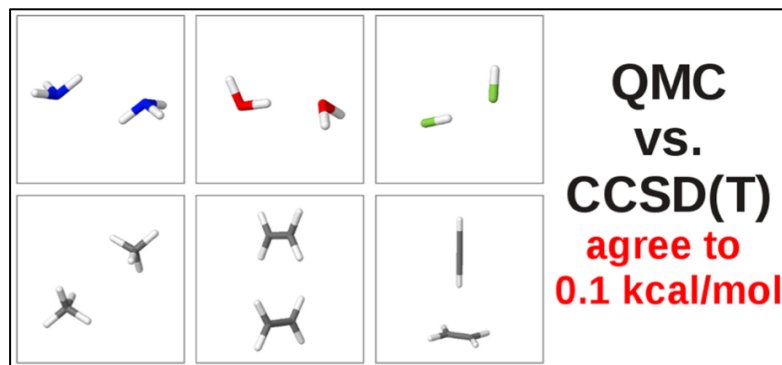
Quick Survey of S-J



Nemec, et al., JCP **132**, 034111 (2010).

S22 Test set (kcal/mol):

PBE:	2.50	MP2:	0.88
PBE0:	2.30	CCSD(T)-CBS:	0
PBE-D3:	0.44	QMC-SJ:	~0.27
B3LYP:	3.66		
B3LYP-D3:	0.36		



complex	reference	FN-DMC ^b	Δ^b	FN-DMC ^c	Δ^c
ammonia dimer	-3.15	-3.19 ± 0.09	0.04	-3.10 ± 0.06	-0.05
water dimer	-5.07	-5.34 ± 0.09	0.27	-5.15 ± 0.08	0.08
hydrogen fluoride dimer	-4.58			-4.68 ± 0.10	0.10
methane dimer	-0.53	-0.48 ± 0.08	-0.05	-0.44 ± 0.05	-0.09
ethene dimer	-1.48	-1.38 ± 0.13	-0.10	-1.47 ± 0.09	-0.01
ethene/ethyne	-1.50	-1.22 ± 0.12	-0.28	-1.56 ± 0.08	0.06
benzene/water	-3.29	-3.69 ± 0.24	0.40	-3.53 ± 0.13	0.24
benzene/methane	-1.45	-0.63 ± 0.21	-0.87	-1.30 ± 0.13	-0.15
benzene dimer T	-2.71	-3.77 ± 0.39	1.06	-2.88 ± 0.16	0.17

Dubecky, et al., JCTC **9**, 4287-4292 (2013).

Multi-Determinant Wave-Functions

$$\Psi_T(\vec{r}) = e^{J(\vec{r})} \sum_k c_k \sum_q d_{k,q} D_{k,q\uparrow}(\vec{r}^\uparrow) D_{k,q\downarrow}(\vec{r}^\downarrow)$$

Multi-Slater Determinant Jastrow

$$CSF_k = \sum_q d_{k,q} D_{k,q\uparrow}(\vec{r}^\uparrow) D_{k,q\downarrow}(\vec{r}^\downarrow)$$

- Configuration State Function (CSF): Space and spin adapted linear combination of Slater determinants.
 - $\{d_q\}$ are determined by symmetry
- Optimize linear coefficients with VMC.
 - Systematic reduction of fixed-node error!
- Limited applicability in extended systems.
 - Expansion is not size-consistent!
- Recover both static and dynamic correlation
 - Jastrow and linear coefficients must be optimized together to obtain optimal results.
 - Efficient and robust optimization algorithms are crucial!

Basic Algorithm

For Local Energy

$$\Psi_T(\vec{r}) = e^{J(\vec{r})} \sum_{k,q} c_k d_{k,q} D_{k,q\uparrow} D_{k,q\downarrow} = e^{J(\vec{r})} A(\vec{r})$$

$$\vec{\nabla}_i A(\vec{r}) = \sum_{k,q} c_k d_{k,q} D_{k,q\uparrow} D_{k,q\downarrow} \vec{\nabla}_i (\ln D_{k,q\uparrow} + \ln D_{k,q\downarrow})$$

$$\nabla_i^2 A(\vec{r}) = \sum_{k,q} a_{k,q} D_{k,q\uparrow} D_{k,q\downarrow} \left(\frac{\nabla_i^2 D_{k,q\uparrow}}{D_{k,q\uparrow}} + \frac{\nabla_i^2 D_{k,q\downarrow}}{D_{k,q\downarrow}} + 2 \left(\vec{\nabla}_i \ln D_{k,q\uparrow} \right) \cdot \left(\vec{\nabla}_i \ln D_{k,q\downarrow} \right) \right)$$

For VMC Optimization

$$\nabla_{c_k} A(\vec{r}) = \sum_q d_{k,q} D_{k,q\uparrow} D_{k,q\downarrow} = CSF(k)$$

Traditionally, evaluate each determinant independently.

- scales linearly with number of determinants.

Fast Algorithm

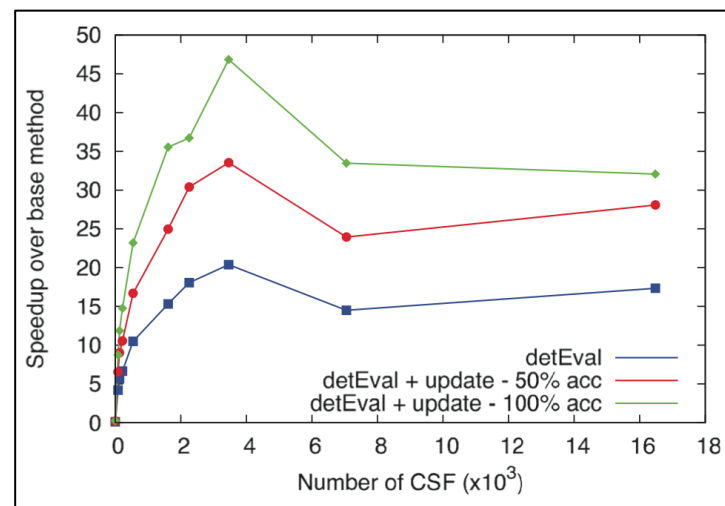
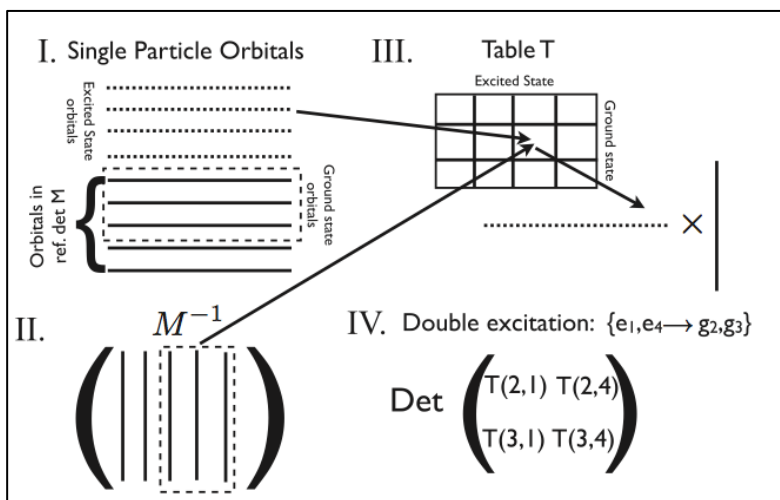
- Instead of evaluating every determinant independently, we can evaluate the ratio of each determinant and a reference determinant using the Generalized Matrix Determinant Lemma.

Matrix Determinant Lemma

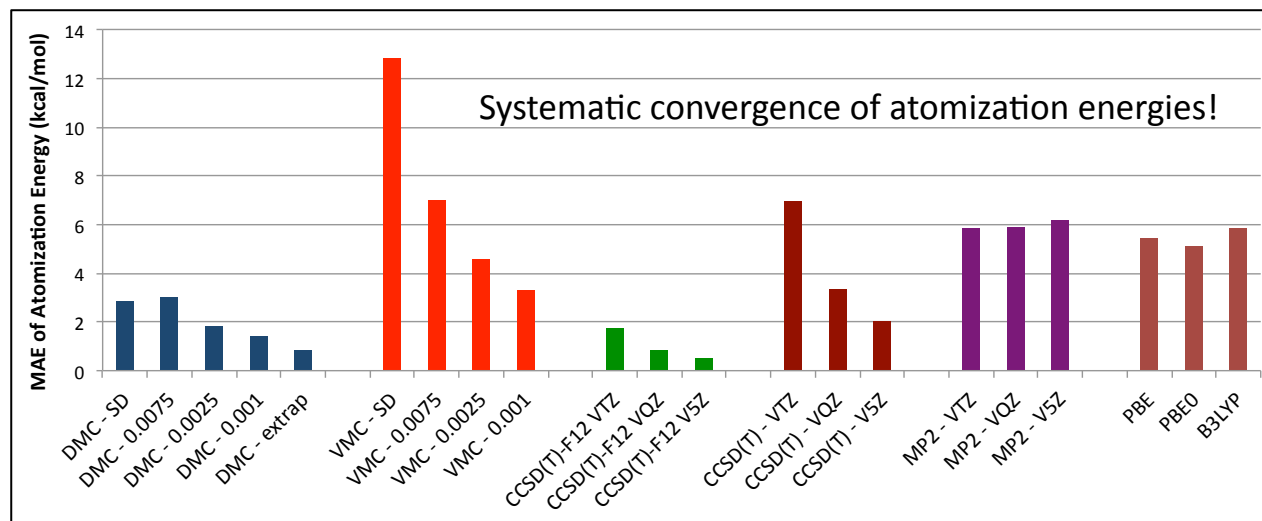
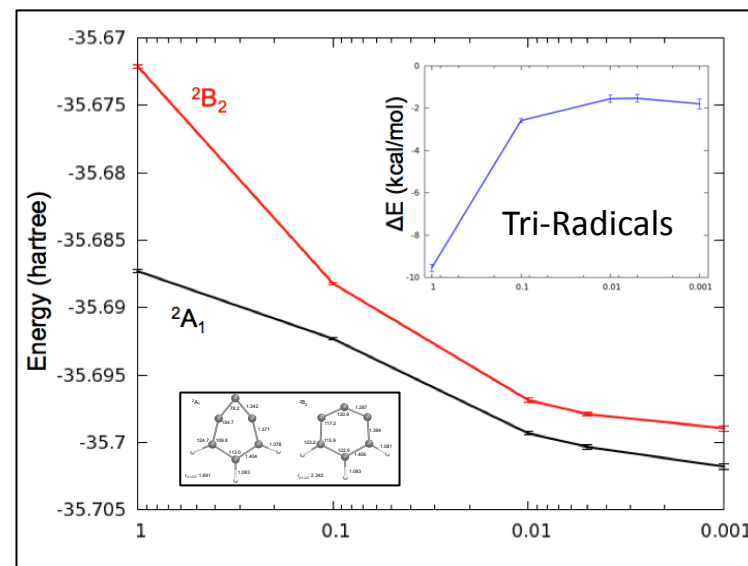
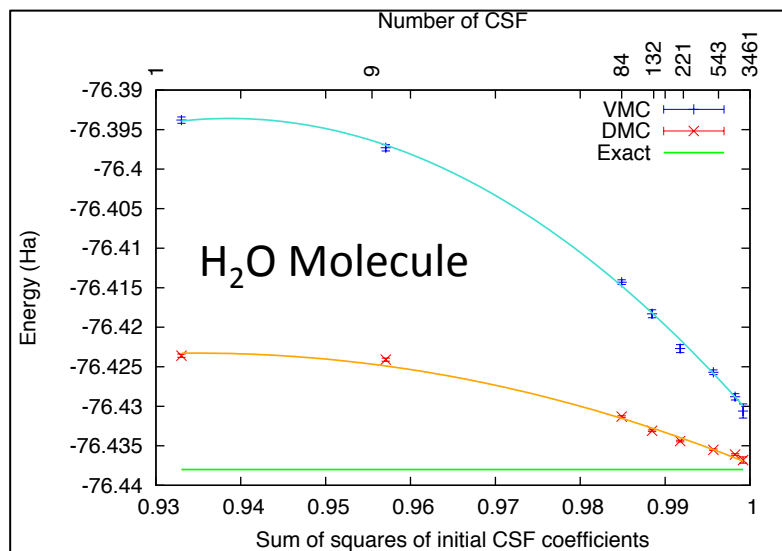
$$\frac{\det(A + uv^T)}{\det(A)} = (1 + v^T Au)$$

Generalized Matrix Determinant Lemma

$$\frac{\det(A + UV^T)}{\det(A)} = \det(1 + V^T AU)$$



Some Applications of MSD



L. Koziol, M. A. Morales, JCP ?? (2014).

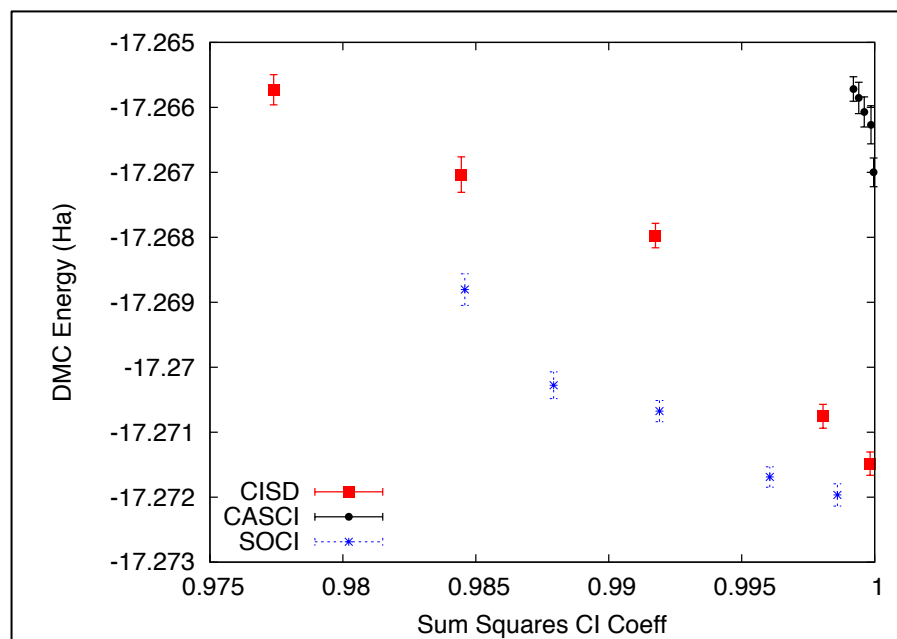
Morales, et al. J. Chem. Theory Comput., 2012, 8 (7), pp 2181–2188

Choice of Orbitals and Configurations

- MSD calculations have 2 important considerations (see afternoon tutorial):
 1. Choice of orbitals
 - Ultimate accuracy of MSD expansion depends on choice of orbitals, e.g. HF, MP2, CASSCF, DFT, ...
 2. Choice of determinant configurations, given 1).
 - No general relation between important configurations across different orbital sets.
 - # of configurations is exponential: currently we rely on QC methods to provide an initial screening.

Challenge to QMC groups: solve within QMC.

1. Calculate optimal orbitals with QMC.
2. Develop efficient screening technique for important determinants.



Backflow Transformations: Operations

1.

$$\mathbf{x}_i^\alpha = \mathbf{r}_i^\alpha + \sum_{j \neq i} \eta(r_{ij}) (\mathbf{r}_i^\alpha - \mathbf{r}_j^\alpha)$$

$$A_{ij}^{\alpha\beta} = \nabla_i^\alpha x_j^\beta$$

$$B_{ij}^\alpha = \nabla_i^2 x_j^\beta$$

2.

$$\varphi_{ki} = \varphi_k(\bar{x}_i)$$

$$\varphi_{ki}^\beta = \frac{\partial \varphi_{ki}}{\partial x_i^\beta}$$

$$\varphi_{ki}^{\alpha\beta} = \frac{\partial^2 \varphi_{ki}}{\partial x_i^\alpha \partial x_i^\beta}$$

3.

$$V_{jk} = (\varphi_{ki})^{-1} = \frac{1}{D} \frac{\partial D}{\partial \varphi_{ki}}$$

$$F_{ij}^\alpha = \sum_k V_{ik} \varphi_{kj}^\alpha$$

4.

$$D = \det(\varphi_{ki})$$

$$\nabla_i^\alpha \ln D = \sum_{\beta, j} F_{jj}^\beta A_{ij}^{\alpha\beta}$$

$$\nabla_i^2 \ln D = \sum_{\alpha, j} B_{ij}^\alpha F_{jj}^\alpha - \sum_{\alpha, \beta, \gamma} \sum_{j, k} A_{ij}^{\alpha\beta} A_{ik}^{\alpha\gamma}$$

$$\times \left(F_{kj}^\beta F_{jk}^\gamma - \delta_{jk} \sum_m V_{jm} \varphi_{mj}^{\beta\gamma} \right)$$

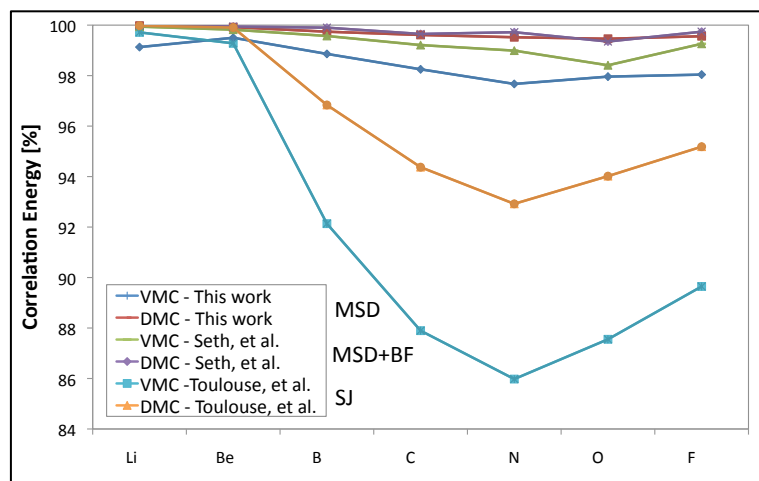
Transformation can be generalized to add electron-ion and three body terms.

Single particle updates change all quasi-particle coordinates.

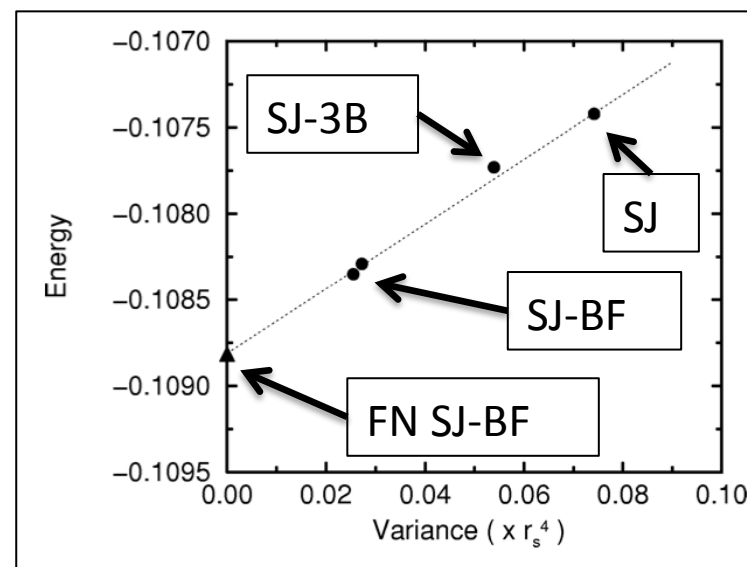
- More expensive evaluation. Single electron moves might still be more efficient!

As seen yesterday, Feynman-Kacs formula naturally leads to two-body Jastrow correlations at first order and at second order to Backflow transformation and three-body Jastrow terms.

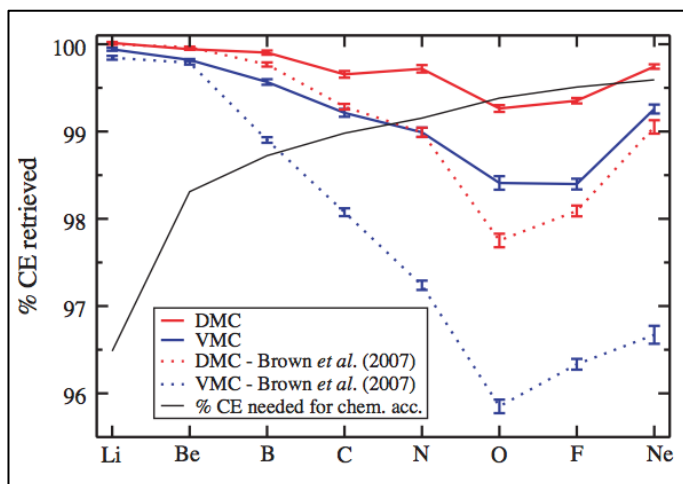
Application of BF and MDF+BF



M.A. Morales, et al. JCTC **8**, 2181-2188 (2012).



Y. Kwon, PRB **58**, 6800 (1998).



Seth, et al. J. Chem. Phys. **134**, 084105 (2011).

- Backflow transformations are very effective for homogeneous systems, e.g. HEG.
- Promising path for molecular systems, in particular when combined with MSD
 - Short MSD expansions (~ 50 - 100 CSF) combined with BF lead to same accuracy as much longer MSD (up to ~ 3000 CSF).
- Typical reduction of variances by $\sim 30\%$ - 50% .

Other Wave-Functions

Exciting developments with novel wave-functions

- Pairing wave-functions
- Controlled determinant expansions

Resonating Valence Bond

$$\Phi_N(\vec{R}) = A \prod_{i=1}^{N/2} \phi(\vec{r}_i^{\uparrow}, \vec{r}_i^{\downarrow})$$

M. Marchi, et al., "Resonating valence bond wave function with molecular orbitals: Application to first-row molecules", JCP 131, 154116 (2009).

Linear-Scaling GVB

$$\Psi_{LGVB1} = c_0 |\Phi_0\rangle + \sum_{i=1}^{N/2} c_i |\Phi_{ib\bar{i}a}^{ia\bar{i}a}\rangle$$

$$\Psi_{LGVB10} = \sum_{ij}^{6n} c_{ij} |\Phi_{ij}\rangle \quad \text{CAS}(4,4)$$

F. Fracchia, et al., "Size-extensive Wave Functions for Quantum Monte Carlo: A Linear-Scaling Generalized Valence Bond Approach", JCTC 8, 1943 (2012).

$$\Psi_{STU} = pf \begin{bmatrix} \xi^{\uparrow\uparrow} & \Phi^{\uparrow\downarrow} & \varphi^{\uparrow} \\ -\Phi^{\uparrow\downarrow T} & \xi^{\downarrow\downarrow} & \varphi^{\downarrow} \\ -\varphi^{\uparrow T} & -\varphi^{\downarrow T} & 0 \end{bmatrix}$$

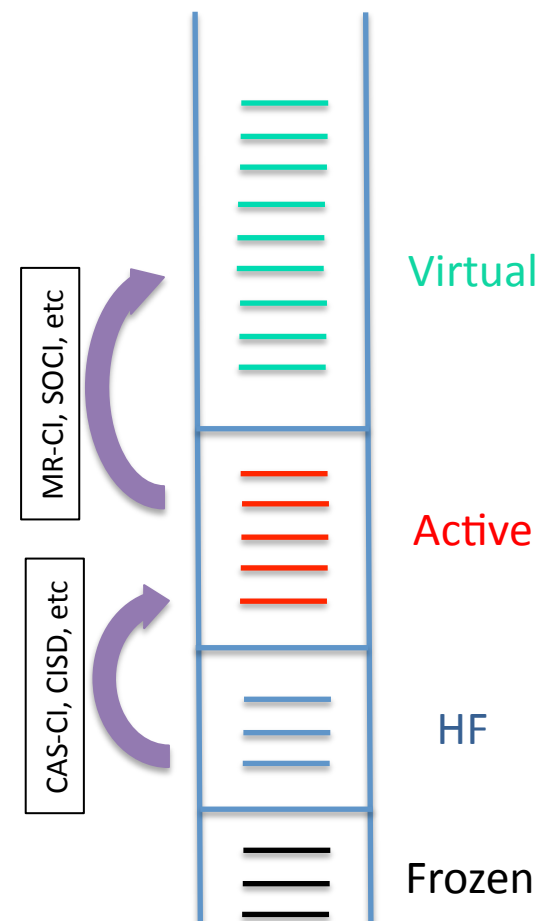
$$\xi_{i,j}^{\uparrow\uparrow} = \sum_{k,l}^M \lambda_{k,l}^{\uparrow\uparrow} \varphi_k(\vec{r}_i^{\uparrow}) \varphi_l(\vec{r}_j^{\uparrow})$$

$\xi^{\uparrow\uparrow}$ = Pairing Matrix

M. Bajdich, et al., "Pfaffian pairing and backflow wavefunctions for electronic structure quantum Monte Carlo methods", PRB 77, 115112 (2008).

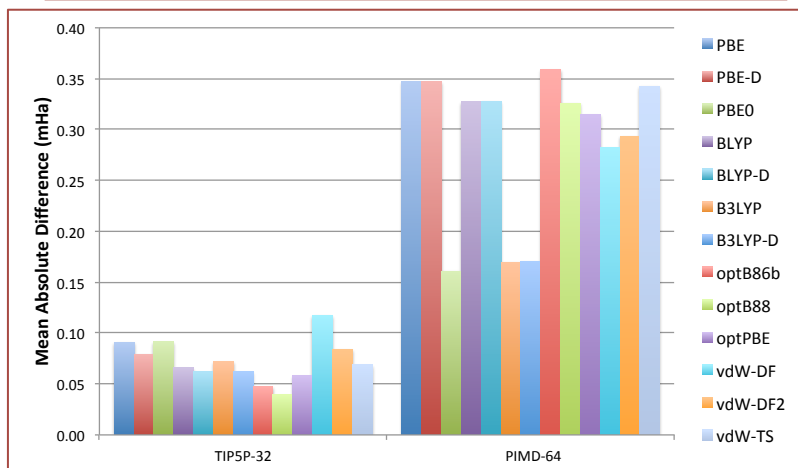
Quantum Chemistry Methods – MCSCF

- Already discussed FCI, Truncated-Cl, CAS-Cl.
 - Performed on a given set of orbitals. Approximate CI methods depend on the set of orbitals.
- Multi-Configuration Self-Consistent Field
 - Combines CI with orbital rotations. Obtains best variational solution within a given wave-function ansatz (selection of determinants).
 - HF orbitals are not optimal for multi-determinant expansions. MCSCF optimizes orbitals for a given expansion!
 - Performs a CI calculation with a selection of determinants. In principle can be very general.
 - CASSCF: Performs calculation on a full CAS. N electrons in M orbitals.
- Multi-Reference CI or Second-Order CI
 - In addition to a selection of orbitals (e.g. CAS), include all excitations from all orbitals up to a given level.

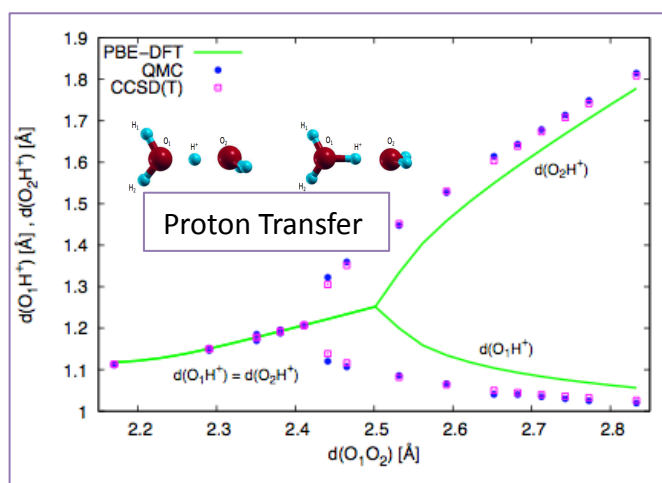


Survey of Some Applications – Water and Aqueous Systems

Benchmark DFT and force fields on bulk systems

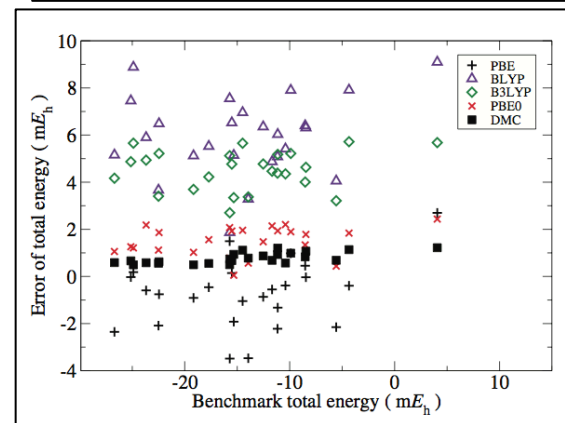


M. A. Morales, et al. JCTC 10, 2355 (2014).



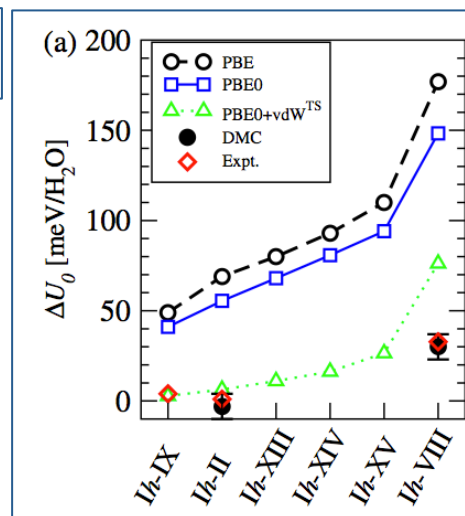
M. Dagrada, et al., <http://arxiv.org/abs/1312.2897>.

Energetics of water clusters



Gillan, et al, J. Chem. Phys. 136, 244105 (2012)

Cohesive energy of ice phases

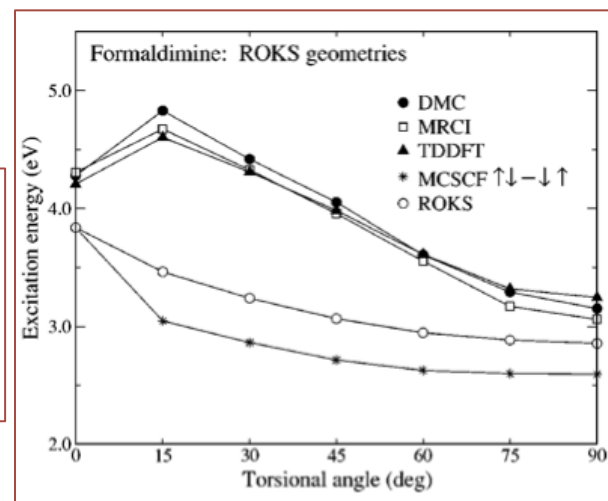
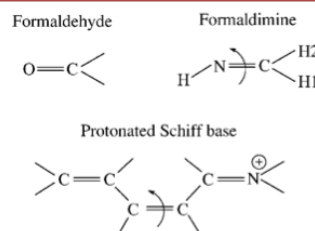


B. Santra, PRL 107, 185701 (2011).

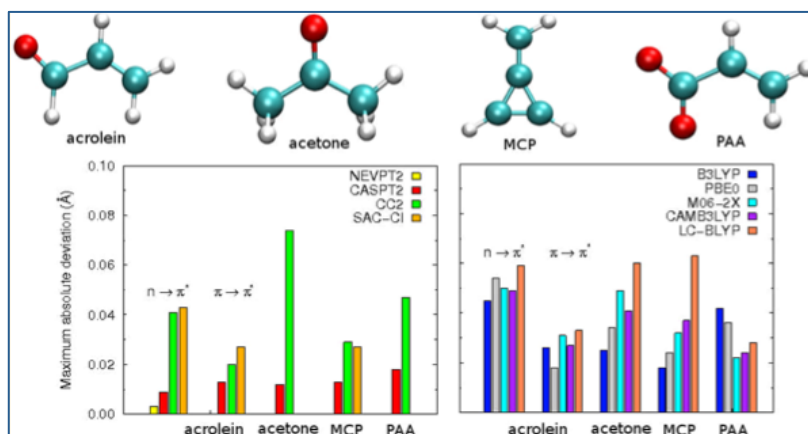
Survey of Some Applications – Excited States

- Recent Development: Direct optimization of excited state wave-functions and geometries
- Many excited states can be very challenging to mean-field methods

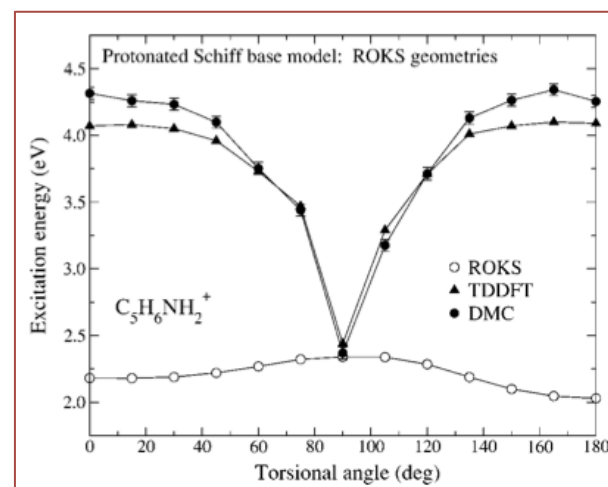
Photo-active biomolecules



Ground and Excited-State Geometry Optimization

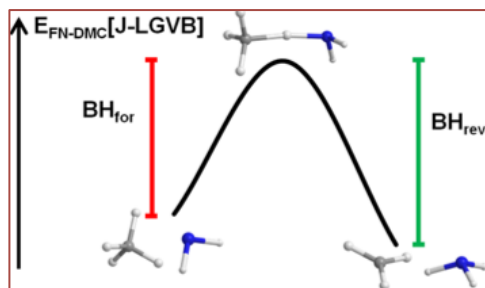


R. Guareschi, et al., "Ground and Excited-State Geometry Optimization of Small Organic Molecules with Quantum Monte Carlo", JCTC 9, 5513 (2013).

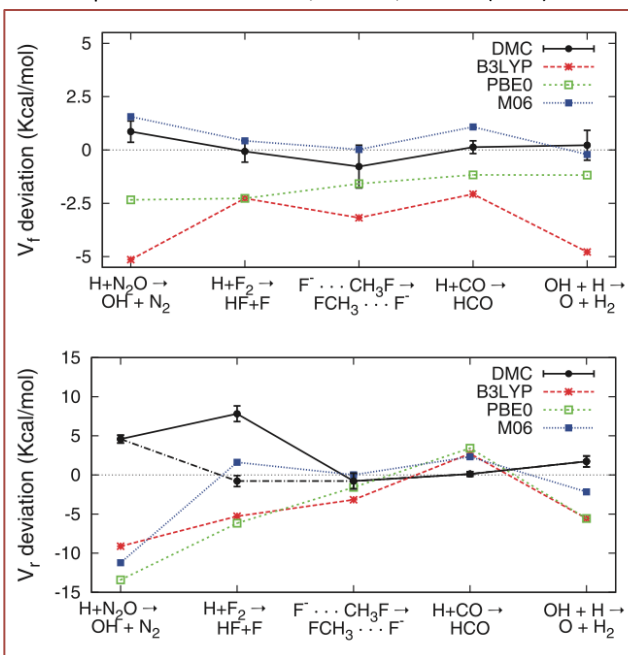


F. Schautz, et al., "Excitations in photoactive molecules from quantum Monte Carlo", JCP 121, 5836 (2004).

Barrier Heights Reaction Pathways

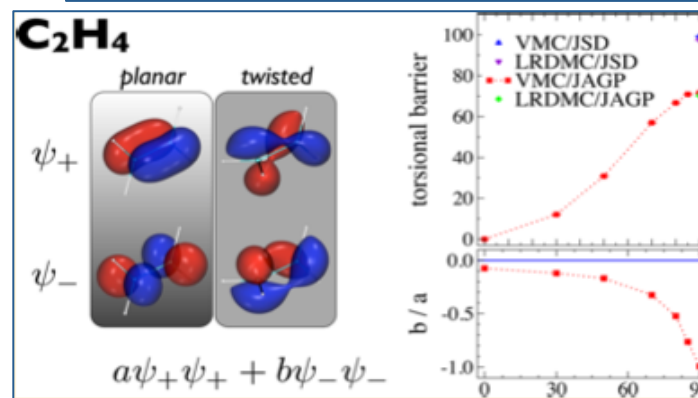


S. Sacconi, et al. "Minimum energy pathways via quantum Monte Carlo", JCP 138, 084109 (2013).



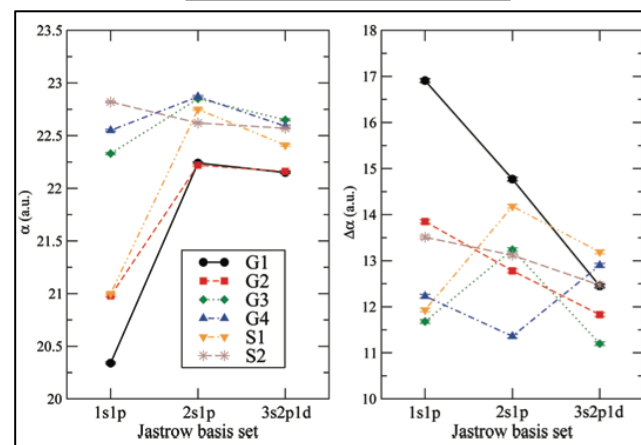
F. Fracchia, et al., "Barrier Heights in Quantum Monte Carlo with Linear-Scaling Generalized-Valence-Bond Wave Functions, JCTC 9, 3453 (2013)."

Di-radical Molecular Systems



A. Zen, et al., "Static and Dynamical Correlation in Diradical Molecules by Quantum Monte Carlo using the Jastrow Antisymmetrized Geminal Power Ansatz", JCTC 10, 1048 (2014).

Polarizabilities



E. Coccia, et al., "Molecular Electrical Properties from Quantum Monte Carlo Calculations: Application to Ethyne", JCTC 8, 1952 (2012).

Outlook – What's the next step?

- Better wavefunctions
 - controlled MSD expansions + BF
 - Orbital and configuration selection within QMC
- More estimators: Forces, second derivatives
- Excitations
- More application!!!
 - Correlated systems.